Biodiesel Oxidation Induction Periods by PDSC

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14. ABSTRACT
This report summarizes experiments with oxidatively reactive methyl soyate biodiesel fuels obtained from different suppliers using different manufacturing processes. Two modified test methods, ASTM E 2009, Standard Test Method for Oxidation Onset Temperature of Hydrocarbons by Differential Scanning Calorimetry, and ASTM D 6186, Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC), were employed as repid tests to correlate to a series of biodiesel samples having a range of stability. Three antioxidants were evaluated for effectiveness and blends of biodiesel in diesel fuel were evaluated using PDSC. The antioxidants were Butylated Hydroxy Toluene (BHT) at 240mg/L,Tertiary Butyl Hydroxy Quinone (TBHQ) at 240 mg/L, and Tenox 21 at 1000 mg/L. Advantages of the ASTM E 2009 method are demonstrated by the ability to get onset temperatures for the biodiesels as well as blends with diesel and the neat diesel and rank the antioxidant effectiveness.

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Outline Of Presentation

- IP & Iodine Value
- Modified ASTM D 5304 & D 2274
- Rapid Oxidation At 146°C (D 5304)
- ASTM D 6186, PDSC @ 125°C
- ASTM E 2009, PDSC @ T-Ramp
- Conclusion

ASTM D 525 Induction Period and Iodine Value For Biodiesels

	Biodiesel (H = High Unsaturates; M = Medium Unsaturates; MH = Medium-High Unsaturates; L = Low unsaturates)			
Test Method	B100(H#3)	B100(H#3/L mix)	B100(M) Ethyl Ester	B100(MH) Ethyl Ester
ASTM D 525, minutes	40	70	1320	620
Iodine Value	122	95	71	101

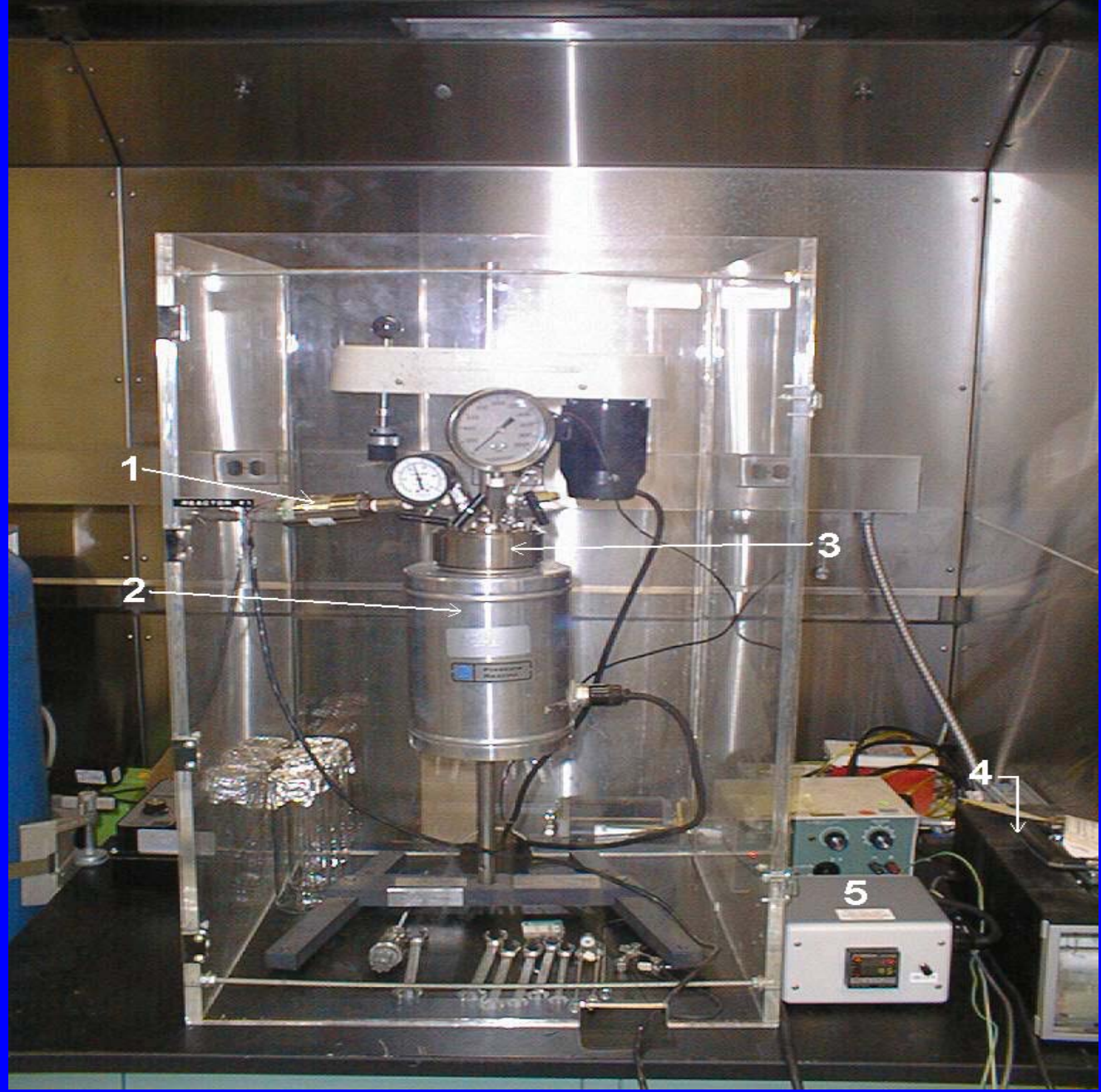
Oxygen Overpressure Reduction & D 2274 Insolubles, TAN and Viscosity Increase

SOY BIODIESELS (H#4, H#5, & H#6); Equivalent IV and olefin distribution
Rancimet Induction Period: ??????????Available

Property	High Unsaturate Sample Number		
	B100(H#4) (Code: 11274)	B100(H#5) (Code: 25842)	B100(H#6) (Code: 26167)
D 5304 Oxygen Overpressure, psig@			
Hour 0	110	114	116
Hour 1	100	114	115
Hour 2	85	112	113
Hour 3	72	112	112
Hour 4	60	110	110
Hour 5	50	110	110
Hour 6	40	109	108
Hour 7	33	108	107
Hour 8	25	107	106
Hour 9	20	106	104
Hour 10	15	105	103
D 2274, modified*			
Insolubles, mg/100mL	14.0	0.1	0.5
TAN, increase mgKOH/g (D 664)	3.6	0.05	0.8
Viscosity increase, mm^2/s (D 445)	2.3	0.05	1.0
*Using Whatman GF/F, isolate filtrate for TAN and viscosity analysis			

ASTM D 5304, 146°C

- Unstable Soy Biodiesel (Methyl Soyate), 100 mL in glass liner
- 100 psig Oxygen
- Reactor Internal Pressure Exceed 200psig at 10 Minutes
- Glass Liner Shattered
- Black Carbon Residue in Vessel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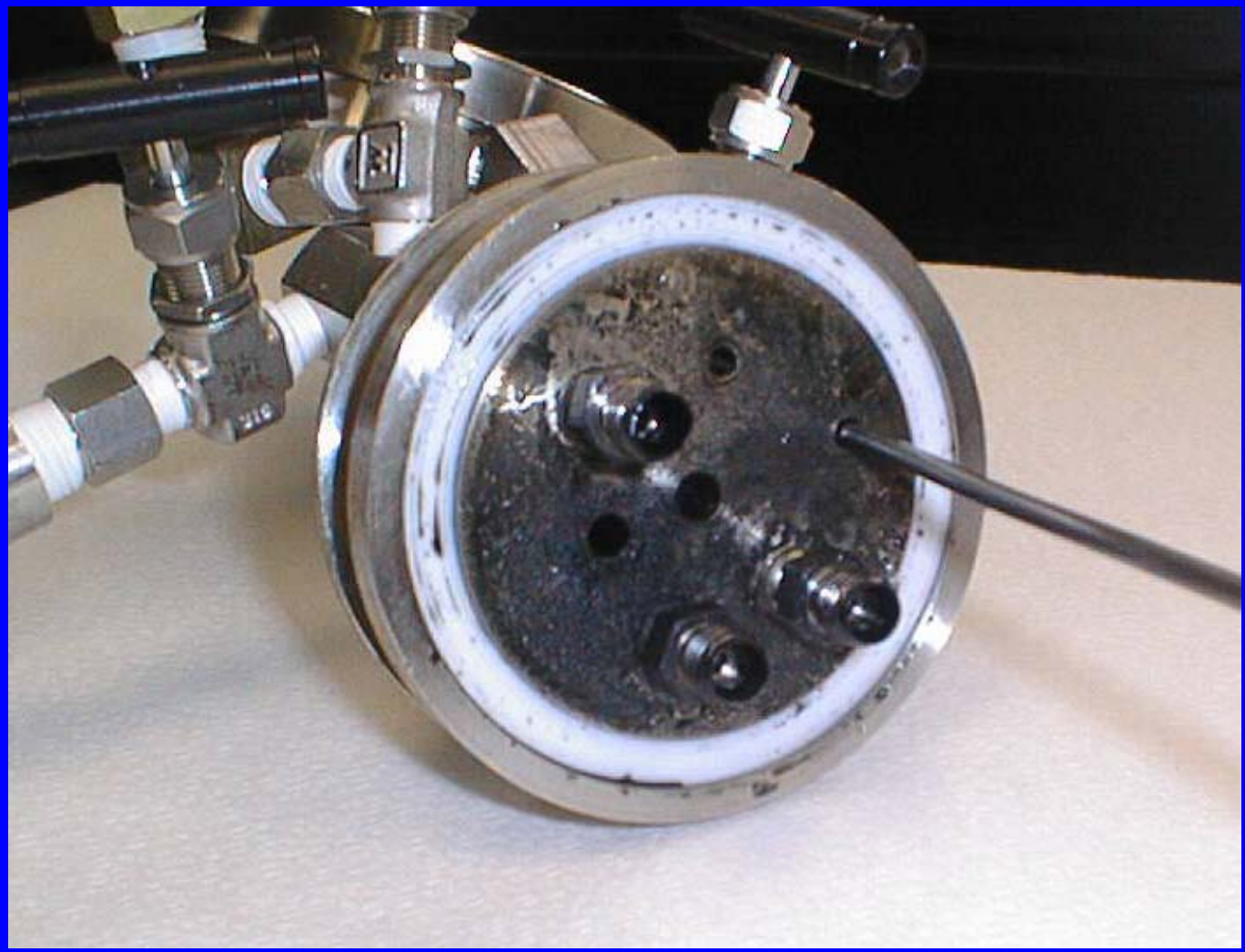
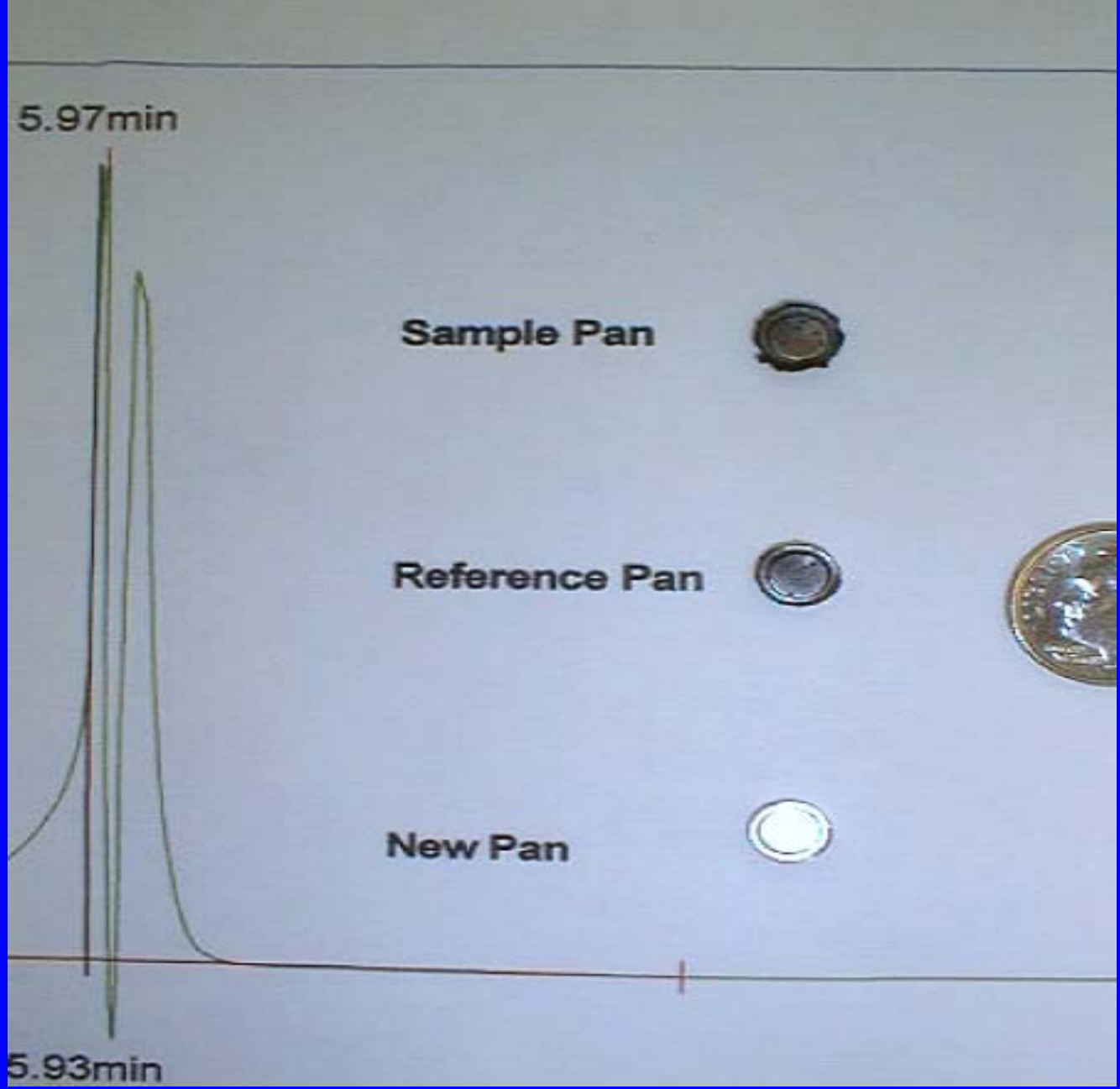
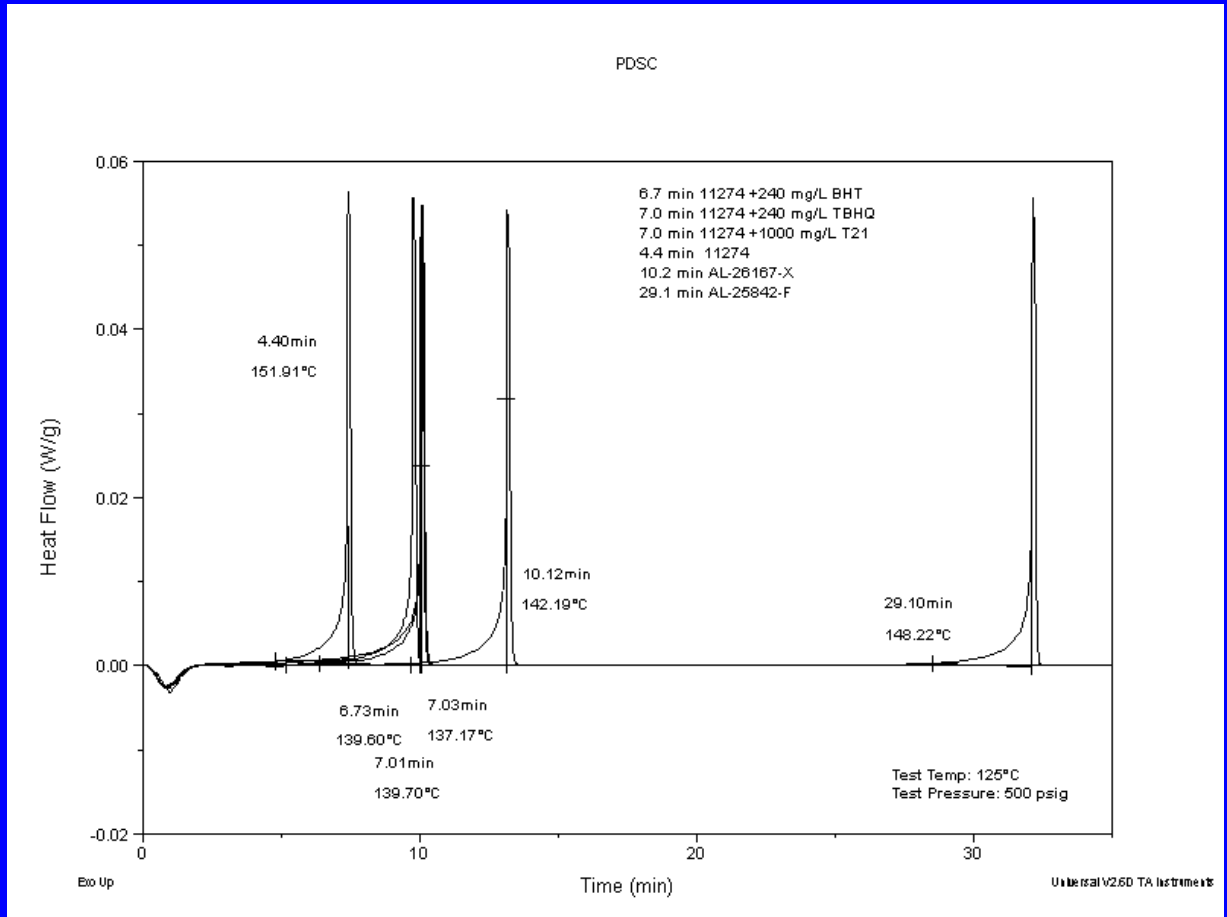


Modified ASTM D 6186

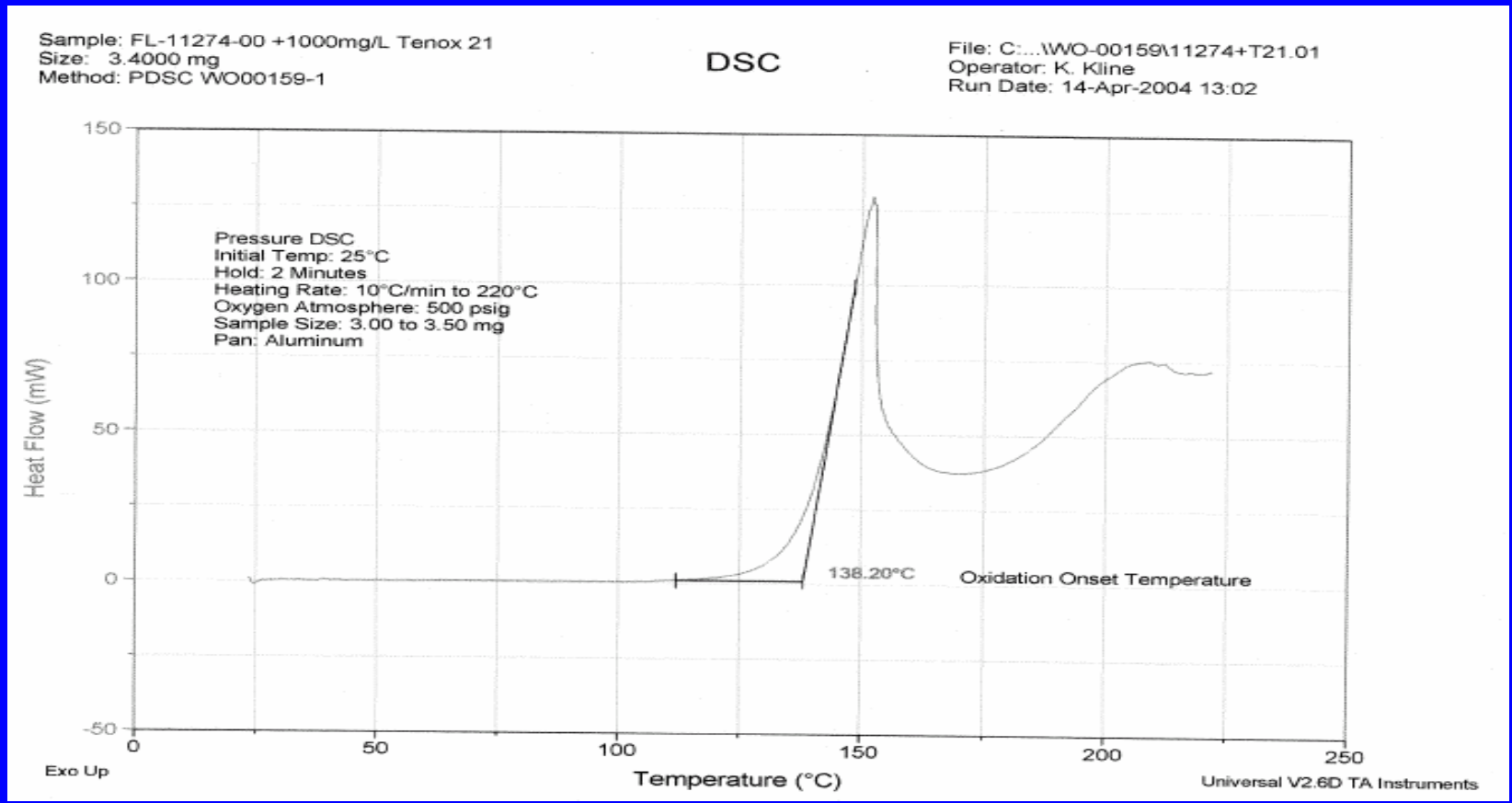
- Pressure Differential Scanning Calorimeter Test At 130°C
- Induction Period Observed At 3.0 Minutes
- Audible Pop at IP
- Carbon Residue On Test Dish
- Further Testing at 125°C Followed


5.97min
Sample Pan
Reference Pan
New Pan
5.93min

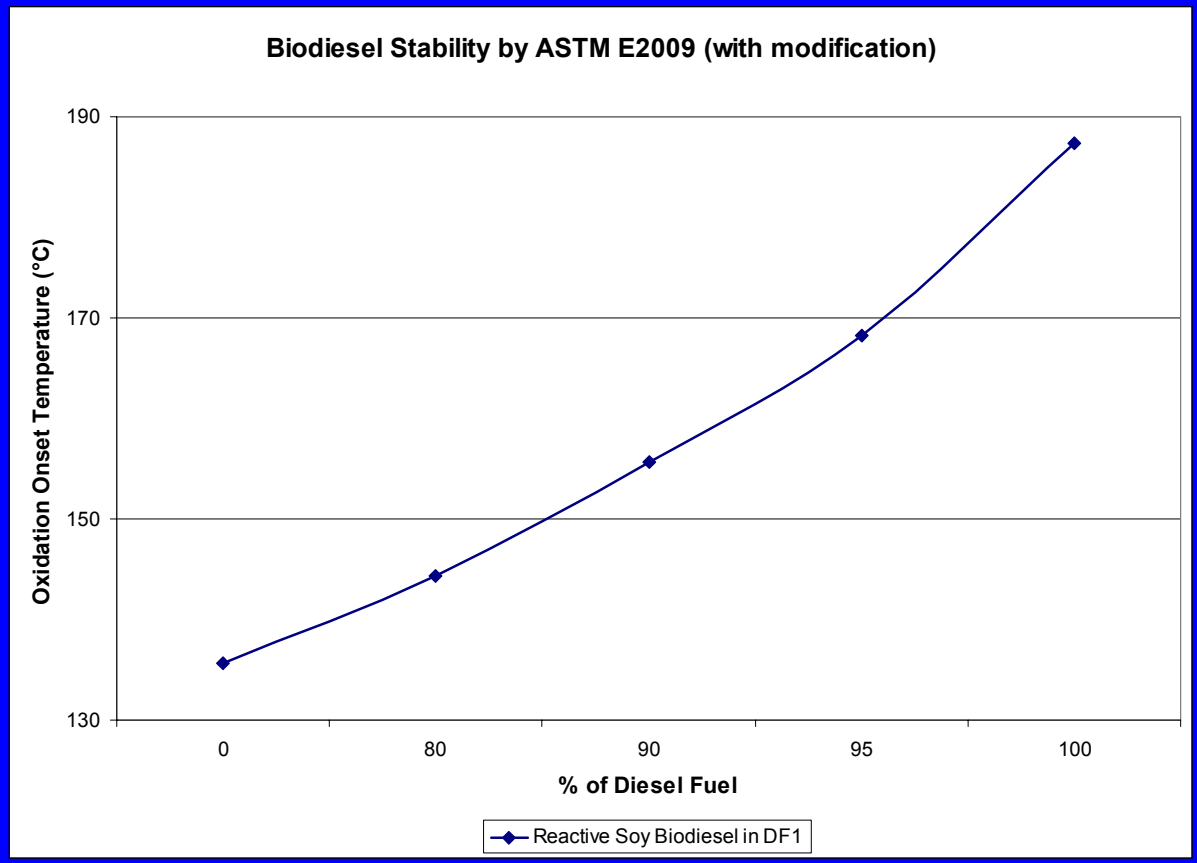
Induction Time by Pressure Differential Scanning Calorimeter at 125°C



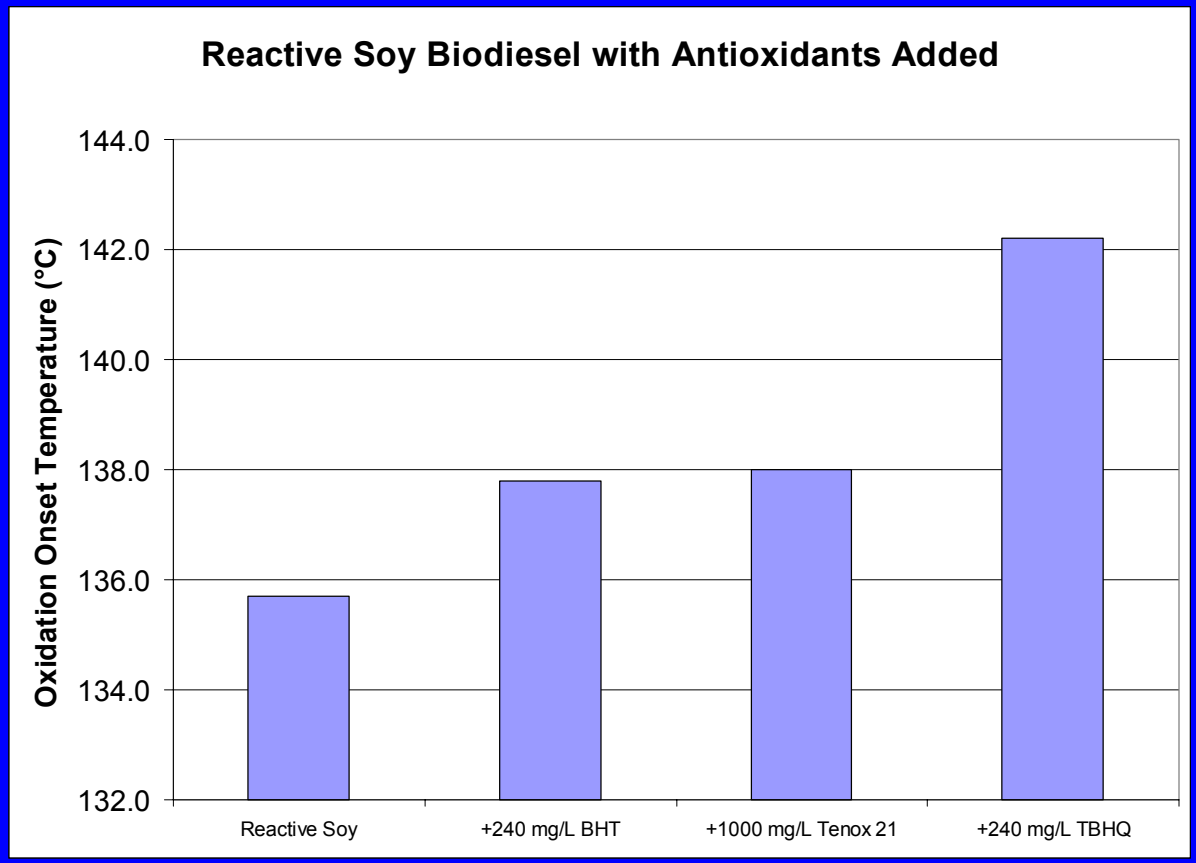
Oxidation Onset Temperature of Hydrocarbons by PDSC



ASTM E 2009 Ramp 10-220 C



Antioxidant Increases Oxidation Onset Temperature



Conclusions & Recommendations

- Soy Biodiesel Oxidative Stability Can Vary Significantly Depending on Commercial Source
- Simple Pressure Differential Scanning Calorimeter Procedure Based On ASTM D 6186 or E 2009 Can Be Used to Determine Induction Period.
- Induction Period Correlates With Other Methods Of Determining Oxidation Stability (e.g. D 5304 & D 2274); (Including Rancimet)
- Modified D 2274 Method Includes Acid Number And Viscosity, Which Increase With Biodiesel Oxidation.
- PDSC Should be Further Investigated For Defining Biodiesel Stability And Flammability Hazard.

References

- SAE Paper Numbers -
  - 1999-01-3520 (Potential Analytical Methods for Stability Testing of Biodiesel and Biodiesel Blends)
  - 2000-01-3422 (Alternative Fuels: Gas to Liquids as Potential 21st Century Truck Fuels)
  - 2000-01-3428 (Alternative Fuels: Development of a Biodiesel B20 Purchase Description)
- Stavinoha, Leo L. and Steve Howell, "Biodiesel Stability Test Methods," presented at IASH 2000 (September 24-29, 2000, at Graz, Austria).
- Diesel Fuel, Biodiesel B20 Commercial Item Description: A-A-59693
- Stavinoha, Leo L., Emilio S. Alfaro, Jill M. Tebbe, and Luis A. Villahermosa, "Biodiesel and Biodiesel Blend Properties Related to Epact Use" presented at IASH 2003 (September 14-19, 2003, at Steamboat Springs, Colorado).

8TH INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS
Steamboat Springs, Colorado
September 14-19, 2003

BIODIESEL AND BIODIESEL BLEND PROPERTIES RELATED TO EPACT USE

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- 3U.S. Army Tank-automotive and Armaments Command, Attn: AMSTA-TR-D/210, 6501 E. 11 Mile Road, Warren, MI 48397-5000 USA
- Biodiesel is defined as "a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats, designated B100" in the American Society for Testing and Materials (ASTM) D 6751 specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels. In 1992, the U.S. Congress enacted the Energy Policy Act (EPAct) requiring federal and state vehicle fleets to purchase alternative fueled vehicles (AFV). EPAct was amended in 1998 as the Energy Conservation and Reauthorization Act (ECRA) to include biodiesel as an option for meeting AFV acquisition requirements by purchasing and using either 450 gallons of biodiesel or 2250 gallons of biodiesel blend consisting of 20% volume biodiesel in petroleum diesel fuel (designated B20). An effort initiated by U.S. Army TACOM/TARDEC/NAC to provide a specification for B20 biodiesel blended fuel for use by Government agencies resulted in publication of Commercial Item Description (CID) A-A-59693, Diesel Fuel, Biodiesel Blend (B20). This report summarizes data developed in a project designed to characterize selected biodiesel samples (identified in market survey, TARDEC Technical Report No. 13801) and biodiesel (B20) blends made with diesel fuels. The biodiesel feed stocks included unused soybean oil, used cooking oil, used soybean cooking oil, unused vegetable oil, used vegetable oil, unused canola oil, unused cottonseed oil, and yellow grease. Various chemical and physical properties were determined to ensure compliance with B20 and B100 specification requirements. The data was instrumental in deciding that the B20 specification should be restricted to one grade of biodiesel blend as the winter grade low sulfur diesel fuel No. 1-D (LS 1-D) has too restrictive of a distillation requirement. The B100 samples were also tested for oxidation stability in accordance with ASTM D 6186 at 125°C, using pressure differential scanning calorimetry (PDSC). The biodiesels having the highest level of unsaturation were the most reactive but ranged considerably depending on source. Biodiesel from used feedstock and all B20 blends did not have measurable induction times at the selected test temperature and are considered to be more oxidatively stable than the soy based biodiesels that had measurable induction times.